(19) Europäisches Patentamt
European Patent Office
Office uropéen d s brevets

(11) Publication number : **0 490 672 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number : 91311555.6

(22) Date of filing : 12.12.91

(51) Int. Cl.^{5}: **C08F 6/08**, C08F 6/24

(30) Priority : 14.12.90 JP 402206/90
18.12.90 JP 403162/90

(43) Date of publication of application :
17.06.92 Bulletin 92/25

(84) Designated Contracting States :
DE FR GB IT NL

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(54) Method of removing catalyst from ethylene-alpha-olefin copolymer.

(57) After a copolymer of ethylene and an alpha-olefin of at least 3 carbon atoms (e.g. propylene) and optionally also a non-conjugated diene has been prepared with the use of a vanadium catalyst and an organoaluminum (e.g. alkyl) compound, the residual catalyst is removed from the polymerisation reaction mixture in a hydrocarbon solvent (e.g. hexane) by

(a) when the catalyst also includes a halogenated ester compound, mixing the reaction mixture with stirring into an aqueous solution of an alkaline compound (e.g. hydroxide of Li, Na or K) in an amount to give an aqueous phase pH of at least 10 ; or

(b) the halogenated ester compound being optional, oxidising the reaction mixture with an oxidising agent (preferably O_2), e.g. to convert the vanadium to pentavalent V, in an aqueous alkaline solution as in (a).

The organic phase is then separated and washed with water and the polymer is recovered therefrom.

The catalyst residue is thus reduced to very low levels, so that the copolymer is not affected thereby.

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This invention relates to a method for purifying ethylene-α-olefin copolymers by removing therefrom catalytic ingredients.

In the preparation of an ethylene-α-olefin copolymer in a hydrocarbon solvent in the presence of a catalyst comprising a vanadium compound and an organo-aluminum compound, or a catalyst comprising a vanadium compound, an organoaluminum compound, and a halogenated ester compound, if the catalytic ingredients remain or are incorporated in the copolymer as a final product, problems such as discoloration of the copolymer and deterioration in weather resistance and heat resistance of the copolymer occur. Hence, the catalytic ingredients remaining in the copolymer obtained by the polymerization reaction must be completely removed from the copolymer.

Conventional methods for removing the catalytic ingredients from the ethylene-α-olefin copolymer prepared in the presence of a vanadium-based catalyst include a method wherein a large amount of water is added to a polymer solution, the mixture is mixed in a mixer, the catalyst is extracted into an aqueous phase, the aqueous phase is separated from an organic phase, and the polymer containing a reduced amount of the catalytic ingredients is recovered from the organic phase; and a method wherein water or an alcohol is added to a slurry obtained by a copolymerization reaction in a solvent which does not dissolve therein the polymer, to reduce the amount of catalytic residue in the polymer [see, Yasuharu Saeki, Polymer Production Process, published by Kogyo Chosakai (1971)].

However, these methods have some disadvantages described below.

In the method wherein a polymer solution is treated with a large amount of water, it is considered that the catalytic ingredients which are solubilized in water by bringing them into contact with water are extracted with water. However, when one expects that the catalytic ingredients are more completely removed, the mixing of the polymer solution with water must be thoroughly made, and a large-size, heavy-duty mixer must be used at a high speed (at high revolution number). Hence, the costs of equipment and power are high and, therefor , the method is not industrially advantageous.

In the method using an alcohol, the alcohol must be purified and reused and, hence, not only is the process complicated, but the energy consumption is increased. Thus, the method also is not industrially advantageous.

As other methods, JP-A-63-275605 ("JP-A" means an unexamined published Japanese patent application) discloses a method wherein copolymers prepared in the presence of a titanium-based catalyst are washed with water containing an alkaline compound; and JP-B-43-6471 ("JP-B" means an examined Japanese patent publication) discloses a method wherein copolymers prepared in the presence of a vanadium-based catalyst are oxidized and then washed with water containing an alkaline compound.

In recent years, since ethylene-α-olefin rubbery copolymers are mixed with other polymers such as polypropylene and are widely used for automobile parts and packaging materials, the requirements for weather resistance and non-discoloration of the rubbery copolymers have become more stringent. In order to meet the requirements, it is highly desirable to further reduce the amount of the catalytic ingredients remaining in th rubbery copolymer. For example, it is required that the amount of the vanadium compound in the copolymer is reduced to not higher than 1 ppm in terms of V_2O_5.

Further, there is a problem that in addition to the metallic catalytic ingredients, halogenated ester compounds (used as activating agents for the polymerization reaction) remain in the copolymer; and this causes problems such as lowering in the quality of the copolymer so that corrosion of processing machines and coloration of the copolymers occur, and the copolymers are no longer useful as vessels and packaging materials for foods and medicines.

Therefore, the conventional purification techniques described in the aforesaid patent specifications are not yet satisfactory.

An object of the present invention is thus to provide a method capable of removing catalytic ingredients, to a level which could not be achieved by conventional methods, in purifying a polymerisation reaction mixture containing an ethylene-α-olefin copolymer obtained by polymerizing ethylene with an α-olefin having at least 3 carbon atoms, or ethylene with an α-olefin having at least 3 carbon atoms and a non-conjugated diene compound, in a hydrocarbon solvent in the presence of a catalyst comprising a vanadium compound and an organoaluminum compound, or a catalyst comprising a vanadium compound, an organoaluminum compound, possibly a halogenated ester compound.

In a first embodiment, the present invention provides a m thod of purifying a polymerisation r action mixture containing an ethylene-α-olefin copolymer obtained by polymerizing ethylene with an α-olefin having at least 3 carbon atoms, or ethylene with an α-olefin having at least 3 carbon atoms and a non-conjugated diene compound, in a hydrocarbon solvent in the presence of a catalyst comprising a vanadium compound, an organo-aluminum compound, and a halogenated ester compound, the method including mixing and stirring a polymerization reaction mixture obtained by the polymerization reaction in an aqueous alkaline solution in such an amount as to give an aqueous phase having a pH of not lower than 10.0 after mixing and stirring.

In a second embodiment, the present invention provides a method of purifying an ethylene-α-olefin copolymer obtained by polymerizing ethylene with an α-olefin having at least 3 carbon atoms, or ethylene with an α-olefin having at least 3 carbon atoms and a non-conjugated diene compound, in a hydrocarbon solvent in the presence of a catalyst comprising a vanadium compound and an organoaluminum compound, the method including treating a polymerization reaction mixture obtained by the polymerization reaction with an oxidizing agent in an aqueous alkaline solution in such an amount as to give an aqueous phase having a pH of not lower than 10.0 after oxidation.

In the said polymerization reaction mixtures to be purified, any solvent or medium in which the copolymer is soluble or insoluble can be used as the hydrocarbon solvent or dispersant. Examples of solvents which can be suitably used include aromatic compounds such as benzene and toluene; aliphatic hydrocarbon compounds such as pentane, hexane and heptane; alicyclic hydrocarbon compounds such as cyclopentane, methylcyclopentane and cyclohexane; α-olefins such as liquefied propylene, liquefied 1-butene and 4-methylpentene-1; and mixtures thereof.

Examples of the vanadium compound which can be used in the present invention include VCl_3, VCl_4, $VOCl_3$ and $VO(OR)_{3-m}Cl_m$ (wherein R is a straight chain or branched alkyl group, a cycloalkyl group or an aryl group, each having 1 to 10 carbon atoms; and $3 \geqq m \geqq 0$), such as $VO(OCH_3)Cl_2$, $VO(OCH_3)_2Cl$, $VO(OCH_3)_3$, $VO(OC_2H_5)Cl_2$, $VO(OC_2H_5)Cl$, $VO(OC_2H_5)_3$, $VO(OC_3H_7)Cl_2$, $VO(OC_3H_7)_2Cl$, $VO(OC_3H_7)_3$, $VO(OisoC_3H_7)Cl_2$, $VO(OisoC_3H_7)_2Cl$, $VO(OisoC_3H_7)_3$, $V(OCH_3)_3$ and $V(OCH_2COOCH_3)_3$.

Examples of the organoaluminum compound which can be used include AlR'_nCl_{3-n} and $AlR'_n(OR')_3$ (wherein R′ is a straight chain or branched alkyl group having 1 to 8 carbon atoms; and $3 \geqq n \geqq 0$), such as $(C_2H_5)_2AlCl$, $(C_4H_9)_2AlCl$, $(C_6H_{13})_2AlCl$, $(C_2H_5)_{1.5}AlCl_{1.5}$, $(C_4H_9)_{1.5}AlCl_{1.5}$, $(C_6H_{13})_{1.5}AlCl_{1.5}$, $C_2H_5AlCl_2$, $C_4H_9AlCl_2$ and $C_6H_{13}AlCl_2$.

A halogenated ester compound which can be effectively used is a compound represented by the following formula:

$$R'' - \underset{\underset{O}{\|}}{C} - O - R'''$$

wherein R″ represents an organic group having 1 to 20 carbon atoms, which is partially or wholly substituted by a halogen atom; and R‴ represents a hydrocarbon group having 1 to 20 carbon atoms. Compounds wherein R″ is wholly substituted by chlorine atoms and compounds having a phenyl group and a chlorine-substituted alkyl group are preferred. More preferred are perchlorocrotonic acid esters, perchloro-3-butenoic acid esters, and phenyldichloroacetic acid esters.

Specific examples of the halogenated ester compound include ethyl dichloroacetate, methyl trichloroacetate, ethyl trichloroacetate, methyl dichlorophenylacetate, ethyl dichlorophenylacetate, methyl perchlorocrotonate, ethyl perchlorocrotonate, propyl perchlorocrotonate, isopropyl perchlorocrotonate, butyl perchlorocrotonate, cyclopropyl perchlorocrotonate, phenyl perchlorocrotonate, methyl perchloro-3-butenoate, ethyl perchloro-3-butenoate, propyl perchloro-3-butenoate and butyl perchloro-3-butenoate.

In addition to these catalytic ingredients, hydrogen, etc. as a molecular weight modifier may be used in the present invention.

Examples of an α-olefin having at least 3 carbon atoms include propylene, 1-butene, 1-pentene, 1-hexene, 4-methylpentene-1, 1-octene and 1-decene.

Examples of the non-conjugated diene compound include dicyclopentadiene, tricyclopentadiene, 5-methyl-2,5-norbornadiene, 5-methylene-2-norbornene, 5-ethylidene-2-norbornene, 5-isopropylidene-2-norbornene, 5-isopropenyl-2-norbornene, 5-(1′-butenyl)-2-norbornene, 5-(2′-butenyl)-2-norbornene, 1,4-hexadiene, 1,6-octadiene and 6-methyl-1,5-heptadiene.

There is no particular limitation with regard to other polymerization conditions than those described above.

The polymerization reaction mixtures to be purified in the present invention can be obtained in the manner mentioned above.

The purification methods of the present invention are now described.

The first embodiment of the present invention is a method of purifying an ethylene-α-olefin copolymer, the method including a step of mixing and stirring the above-described polymerization reaction mixture in an aqueous alkaline solution in such an amount as to give an aqueous phase having a pH of not lower than 10.0 after mixing and stirring.

This method preferably comprises the following two steps.

First step: the polymerization reaction mixture is mixed and stirred in an aqueous solution containing an

alkaline compound in such an amount that an aqueous phase separated in the subsequent second step has a pH of not lower than 10.0.

Second step: the mixture obtained in the first step is separated into an aqueous phase and an organic phase, and the organic phase is washed with neutral water.

This embodiment can alternatively comprise the following three steps:

First step: the polymerization reaction mixture obtained by the polymerization reaction is mixed and stirred in an aqueous solution containing an alkaline compound in such an amount that an aqueous phase formed in the subsequent second step has a pH of not lower than 10.0.

Second step: one part by volume of the mixture obtained in the first step is mixed with 1/5 to 10 parts by volume of neutral water.

Third step: the mixture obtained in the second step is separated into an aqueous and an organic phase, and the organic phase is washed with neutral water.

In a preferred manner for adding the aqueous alkaline solution in this first embodiment, an aqueous alkaline solution having a pH of not lower than 12, and preferably not lower than 13, is used, 1/1000 to 10 parts by volume of the aqueous alkaline solution is added to and mixed with one part by volume of the polymerization reaction mixture with stirring, and 1/5 to 10 parts by volume of water is additionally added thereto and mixed therewith to separate the mixture into an oily phase and an aqueous phase.

As mentioned above, water must be added in an amount sufficient to extract therewith ashes (deposit) mainly formed from the catalytic ingredients and to separate the mixture into an organic phase and an aqueous phase. Specifically, the amount of water added is 1/5 to 10 parts by volume, and preferably 1/4 to 5 parts by volume, per part by volume of the polymerization reaction mixture.

It is preferred that water to be added has an iron content as low as possible. When iron components are present in the water, the desired copolymer is apt to be colored. Preferably, the concentration of the iron components is not higher than 0.1 ppm.

The important characteristic feature of this first embodiment resides in mixing and stirring the polymerization reaction mixture with the aqueous alkaline solution. When the halogenated ester compound is treated with an aqueous alkaline solution having a relatively high pH value, the compound is easily decomposed and extracted into the aqueous phase; but the decomposition reaction of the halogenated ester compound proceeds very slowly at a pH of not higher than 10.0 or under neutral or acidic conditions, and it is then substantially impossible to completely decompose and remove this compound.

Further, the treatment with the aqueous alkaline solution does not interfere with the decomposition and extraction of the residue of the vanadium compound and organoaluminum compound-based catalyst but rather has an effect of accelerating the decomposition and extraction thereof. Accordingly, the purification method of the present invention is very effective as a method for decomposing and removing both the metallic catalyst reside and the halogenated ester compound.

The second embodiment of the present invention is a method of purifying an ethylene-α-olefin copolym r, the method including an oxidation treatment of the above-described polymerization reaction mixture in an aqueous alkaline solution in such an amount as to give an aqueous phase having a pH of not lower than 10.0 after the oxidation treatment.

This method preferably comprises the following first and second steps.

First step: the polymerization reaction mixture is oxidized with an aqueous solution containing an oxidizing agent in at least a stoichiometric amount required for oxidizing vanadium present in the polymerization reaction mixture to a pentavalent state and an alkaline compound in such an amount that an aqueous phase separated in the subsequent second stage has a pH of not lower than 10.0.

Second step: the mixture obtained in the first step is separated into an aqueous phase and an organic phase, and the organic phase is washed with neutral water.

The second embodiment of the method can alternatively comprise the following three steps:

First step: the polymerization reaction mixture obtained by the polymerization reaction is mixed and stirred in an aqueous solution containing an alkaline compound in such an amount that an aqueous phase formed in the subsequent second stage has a pH of not lower than 10.0.

Second step: 1/5 to 10 parts by volume of water containing an oxidizing agent in at least a stoichiometric amount required for oxidizing vanadium in the polymerization reaction mixture to a pentavalent state is added to one part by volume of the mixture obtained in the first step.

Third step: the mixture obtained in the second step is separated into an aqueous phase and an organic phase, and the organic phase is washed with neutral water.

Examples of the alkaline compound which can be used in either embodiment include lithium hydroxide, sodium hydroxide, potassium hydroxide, concentrated ammonia and ammonium hydroxide. Among then, lithium hydroxide, potassium hydroxide and sodium hydroxide are particularly preferred. The alkaline com-

pound must be used in an amount sufficient to give an aqueous phase having a pH of not lower than 10, and preferably not lower than 11, the aqueous phase being separated from the organic phase after the oxidation treatment. When the amount of the alkalin compound is insufficient, the removal of the catalytic ingredients is insufficient.

A preferred way for adding the alkaline compound in the second embodiment is that an aqueous alkaline solution having a pH of not lower than 12, and preferably not lower than 13, is used, and 1/1000 to 10 parts by volume of the aqueous alkaline solution is added to and mixed with one part by volume of the polymerization reaction mixture.

Examples of the oxidizing agent which can be used in the second embodiment include alkali metal nitrites, persulfates, peroxides, hypochlorites, oxygen, ozone and air, such as sodium nitrite, potassium nitrite, hydrogen peroxide or hydroxylamine hydrochloride. Among them, air or oxygen is particularly preferred as the oxidizing agent because not only is air or oxygen easy to handle, but there is no risk that any air or oxygen remains in the copolymer. The oxidizing agent is used in at least a stoichiometric amount required for oxidizing all of the vanadium present in the polymerization reaction mixture to a pentavalent state. When the amount of the oxidizing agent is insufficient, the removal of the catalytic ingredients can be insufficient, and the desired effect of the present invention is not obtained. When the oxidizing agent is used in an amount of twice or more the stoichiometric amount, the valence of all the vanadium can be brought to a pentavalent oxidation state; pentavalent vanadium is colorless and transparent and, hence, the final product copolymer can be completely prevented from being colored. However, when an oxidizing agent other than oxygen is excessively used, the oxidizing agent remains in the final product copolymer. Hence, it is desirable that oxidizing agents other than oxygen are used in an amount of 10 times or less the stoichiometric amount. There is no fear that oxygen remains in the copolymer, even when oxygen is excessively used. However, when a large excess amount of oxygen is used in the continuous polymerization process (including a solvent recycling process), oxygen is accumulated in the solvents, and the copolymer is oxidized and deteriorated. Hence, it is desirable that oxygen is used in an amount of 50 times or less the stoichiometric amount. However, when an oxidizing agent-removing process is provided in an after-stage, such consideration is not required.

In the oxidation treatment, water is used in an amount sufficient to effectively extract therewith ashes mainly formed from the catalytic ingredients and to separate the organic phase and the aqueous phase. Specifically, water is used in an amount of preferably 1/5 to 10 parts by volume, and more preferably 1/4 to 5 parts by volume per part by volume of the polymerization reaction mixture.

It is preferred that water to be used has an iron content as low as possible. When iron components exist in water, the desired copolymer is apt to be colored. Preferably, the concentration of the iron components is not more than 0.1 ppm.

In either embodiment, the mixing and stirring or treatment of the polymerization reaction mixture with an aqueous alkaline solution or an aqueous alkaline solution containing an oxidizing agent may be carried out by using any method, so long as the catalytic ingredients can be efficiently brought into contact with these solutions so as to extract the catalytic ingredients into the aqueous phase. For example, a method using a line mixer can be used. As a method for separating the aqueous phase and the organic phase, a method using a stationary separating drum can for example be used. A step of mixing and stirring or treating the polymerization reaction mixture with the aqueous alkaline solution or the aqueous alkaline solution containing an oxidizing agent and the step of separating the aqueous and organic phases are carried out at a temperature of generally 20 to 160°C, and preferably 50 to 100°C under a pressure of 1 to 20 kg/cm^2G, and preferably 2 to 10 kg/cm^2G. Preferably after the phase separation is carried out, water washing is carried out several times.

The thus obtained organic phase containing the desired copolymer is subjected to a conventional aft r-treatment stage. For example, the hydrocarbon solvent is distilled off by evaporation upon heating, and the residue is dried to obtain the desired ethylene-α-olefin copolymer.

While the features of the second embodiment have been described above, the important characteristic feature thereof resides in the oxidation treatment in an aqueous alkaline solution. The significance thereof is as follows.

When the polymerization reaction mixture is treated with an aqueous alkaline solution, a water-insoluble lowvalent vanadium compound remains in the organic phase. When the vanadium compound is oxidized with an oxidizing agent to a pentavalent state, since a hydroxide of pentavalent vanadium has good solubility in water, the hydroxide of pentavalent vanadium migrates into the aqueous phase and is removed from the organic phase. On the contrary, when the polymerization reaction mixture is subjected to the oxidation treatment under neutral or acidic conditions, an oxide of vanadium is formed; this compound has poor solubility in water even under alkaline conditions and migrates with difficulty into the aqueous phase and, hence it is difficult to remove the compound. As a result, the vanadium compound remains in the desired copolymer. The organoaluminum compound and the halogenated ester compound as a polymerization activator can be decomposed and ext-

racted into the aqueous phase when treated with an aqueous alkaline solution. The oxidation treatment does not interfere with the extraction of the vanadium compound but rather has an effect of accelerating the extraction of the vanadium compound into the aqueous phase.

The present invention is now illustrated in greater detail by reference to the following examples, of which Examples 1 to 8 illustrate the first embodiment and Examples 9 to 14 the second embodiment.

The examples show the removal of the catalytic ingredients to low levels not hitherto obtainable.

EXAMPLE 1

Ethylene and propylene were copolymerized in the presence of a catalyst comprising vanadium oxytrichloride, ethylaluminum sesquichloride, and BPCC (manufactured by Marine Crott, U.S.A, n-butyl perchlorocrotonate according to a catalog of said company) by a conventional method (e.g., the method described in JP-B-44-9390) to prepare a hexane solution containing an ethylene-propylene copolymer.

This uniform hexane solution (containing about 8 wt% of the copolymer) of the ethylene-propylene copolymer (ethylene content: 73 wt%) contained 47 ppm of V_2O_5, 560 ppm of Al_2O_3, 700 ppm of Cl, and about 110 ppm of BPCC, calculated as the copolymer.

To 1000 ml of the hexane solution of the copolymer was added 500 ml of an aqueous sodium hydroxide solution having a pH of 13. The mixture was mixed with stirring at 60°C under atmospheric pressure in a mixer (at 10000 rpm) for 5 minutes. After the mixture was left to stand for about 10 minutes to separate an aqueous phase, the pH of the aqueous phase was measured and found to be 12.6. A 50 ml portion was sampled from the separated oily phase and poured into 50 ml of methanol with stirring to remove the copolymer. The amount of BPCC remained in the thus obtained hexane-methanol mixed solution was quantitatively determined by means of gas chromatography (measuring conditions being described below). To the remainder of the oily phase was added 500 ml of pure water. The mixture was mixed with stirring in a mixer (10000 rpm) for 5 minut s and then left to stand to separate the oily phase. Hexane was distilled off from the oily phase by heating to isolate the copolymer. The content of ashes in the copolymer was determined by means of X-ray fluorometry. The coloration of the copolymer was visually evaluated. No odor based on the halogenated ester compound, etc. was detected at all. The results are shown in Table 1.

Gas chromatographic measurement conditions

Type of device: Hitachi Gas Chromatograph 663-50
Column: 3 mm diameter x 3 m SE-30
Detection: FID 200°C
Temperature rise condition:
100°C constant (10 min) → elevated at a heating rate of 20°C/min (for 5 min) to 200°C → 200°C constant (15 min)
Retention time:
BPCC: 24.5 minutes
Ethyl dichlorophenylacetate: 22 minutes
Methyl trichloroacetate: 7.7 minutes

EXAMPLES 2 TO 5 AND COMPARATIVE EXAMPLES 1 AND 2

The procedures of Example 1 were repeated except that the type of the halogenated ester compound and the pH of the aqueous alkaline solution for use in the mixing and stirring treatment were changed. The results are shown in Table 1.

EXAMPLE 6

An aqueous alkaline solution (NaOH content: 1.25 mol/ℓ, pH: at least 14) formed by dissolving 5 g of sodium hydroxide in 100 ml of water was added to 1000 ml of the hexane solution of the copolymer prepared in Example 1. The mixture was mixed with stirring at 60°C under atmospheric pressure in a mixer (10000 rpm) for 5 minutes.

Subsequently, 500 ml of pure water was added thereto, and the mixture was mixed with stirring in a mixer (10000 rpm) for an additional 5 minutes. After the mixture was left to stand for about 10 minutes to separate an aqueous phase, the pH of the aqueous phase was measured and found to be 13.6. The amount of BPCC remained in the oily phase was quantitatively determined in the same manner as in Example 1. To the separated oily phase was added 500 ml of neutral pure water, and the mixture was mixed with stirring in a mixer (10000

rpm) for 5 minutes to carry out washing. Hexane was distilled off by heating, and the content of ashes was determined by means of X-ray fluorometry. The coloration of the copolymer was visually evaluated. The results are shown in Table 2.

EXAMPLES 7 AND 8 AND COMPARATIVE EXAMPLE 3

The procedures of Example 6 were repeated except that the pH of the aqueous alkaline solution was changed. The results are shown in Table 2.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Comp. Ex. 1	Comp. Ex. 2
Aqueous alkaline solution							
Alkaline compound	NaOH	NaOH	NaOH	NaOH	NaOH	NaOH	omitted
Concentration (mol/ℓ)	0.1	0.03	0.01	0.03	0.03	3×10^{-4}	0
pH	12.6	11.9	10.6	11.8	12.0	10,5	6.7
Amount of aqueous alkaline solution (ml)	500	500	500	500	500	500	500
pH of aqueous phase after separation of oily phase and aqueous phase (pH)	12.6	11.9	10.6	11.8	12.0	9.0	4.5
Halogenated ester compound (1)	BPCC	BPCC	BPCC	DCPAE	TCAM	DCPAE	BPCC
Residual amount of halogenated ester (in hexane) ppm (2)	none	none	none	none	none	8	11
Evaluation of copolymer after purifying							
V_2O_5 (ppm)	<1	2	2	<1	<3	5	15
Al_2O_3 (ppm)	6	8	14	6	10	35	70
Cl (ppm)	18	21	15	24	15	35	45
Color	white	white	white	white	white	pale yellow	pale yellow
Odor	odor-less	odor-less	odor-less	odor-less	odor-less	ester odor	slightly ester odor

(1) BPCC: n-butyl perchlorocrotonate
DCPAE: ethyl dichlorophenylacetate
TCAM: methyl trichloroacetate

(2) None: The peaks of the halogenated ester and the decomposition product thereof were not detected.

Table 2

	Example 6	Example 7	Example 8	Comp. Ex. 3
Aqueous alkaline solution				
Alkaline compound	NaOH	NaOH	NaOH	NaOH
Concentration (mol/ℓ)	1.25	0.08	0.05	0
pH	>14	12.9	12.7	7.0
Amount of aqueous alkaline solution (ml)	100	100	100	100
Amount of water additionally added (ml)	500	500	500	500
pH of aqueous phase after separation of oily phase and aqueous phase (pH)	13.6	11.4	10.5	4.3
Halogenated ester compound (1)	BPCC	BPCC	BPCC	BPCC
Residual amount of halogenated ester (in hexane) ppm (2)	none	none	none	10
Evaluation of copolymer after purifying				
V_2O_5 (ppm)	<1	<1	<1	13
Al_2O_3 (ppm)	4	8	6	65
Cl (ppm)	3	5	4	48
Color	white	white	white	pale yellow
Odor	odorless	odorless	odorless	slightly ester odor

(1) and (2) being the same as in Table 1.

EXAMPLE 9

To 2000 ml of the hexane solution of the copolymer prepared in Example 1 was added an aqueous alkaline solution (NaOH content: 1.25 mol/ℓ, pH: at least 14) formed by dissolving 10 g of sodium hydroxide in 200 ml of pure water (saturated with air and having air dissolved therein under atmospheric pressure; iron content:

0.1 ppm or less). The mixture was mixed with stirring in a nitrogen atmosphere at 60°C under a pressure of 0 kg/cm^{2}G in a mixer (12000 rpm) for 5 minutes. After stirring, 500 ml of pure water (saturated with air and having air dissolved therein under atmospheric pressure) was further added, and the mixture was mixed with stirring in a mixer (12000 rpm) for an additional 5 minutes. After the mixture was left to stand for about 10 minutes to separate an aqueous phase, the pH of the aqueous phase was measured and found to be 13.4. To the separated oily phase was added 500 ml of neutral pure water, and the mixture was mixed with stirring in a mixer (12000 rpm) for 5 minutes to carry out washing. Hexane was distilled off from the oily phase by heating to isolate the copolymer. The content of ashes in the copolymer was determined by means of X-ray fluorometry. The coloration of the copolymer was visually evaluated. The results are shown in Table 3.

EXAMPLES 10 AND 11

The procedures of Example 9 were essentially repeated except that the concentration of the aqueous alkaline solution and the amount thereof to be added were changed. The results together with conditions are shown in Table 3.

COMPARATIVE EXAMPLE 4

The procedures of Example 9 were essentially repeated except that the aqueous alkaline solution was omitted. The results are shown in Table 3.

EXAMPLE 12

Into a 50 liter-volume polymerizer were continuously introduced 913 g/hr of ethylene, 1630 g/hr of propylene, 4.08 ℓ/hr of hexane, 0.32 mmol/hr of vanadium oxytrichloride, 6.8 mmol/hr of ethylaluminum sesquichloride and 0.28 g/h of BPCC (manufactured by Marine Crott, U.S.A.) as a polymerization activator. While 7.2 ℓ/hr of hydrogen as a molecular weight modifier was fed to the mixture, a polymerization reaction was carried out at a temperature of 50°C under a pressure of 13 kg/cm^{2}G. The reaction mixture in the polymerizer was continuously drawn out so that the volume of the reaction mixture in the polymerizer was controlled to 25 liters. The drawn-out reaction mixture was led to a flash drum where the reaction mixture was flashed at a temperature of 60°C under a pressure of 0.8 kg/cm^{2}G to thereby remove the monomer gases. In order to maintain the temperature of the flashed solution, heated hexane was added. To 11.6 kg/hr (about 18 ℓ/hr) of the thus obtained polymerization mixture was added an aqueous sodium hydroxide solution (concentration: 0.16 mol/ℓ, pH: 13.2) at a rate of 200 ml/hr. The mixture was mixed in a mixer. Subsequently, 5 ℓ/hr of water saturated with air (deaerated pure water was saturated with air at a temperature of 20°C under a pressure of 1 kg/cm^{2}G, iron content: 0.1 ppm or less) was added to the mixture. The mixture was mixed in a mixer, and an organic phase was separated from an aqueous phase in a stationary separation drum. The organic phase was washed with water to obtain the final organic phase. Hexane was then distilled off from the final organic phase by flash distillation. The residue was dried to obtain an ethylene-propylene copolymer. The contents of Cl, Al_2O_3 and V_2O_5 in the copolymer were determined by X-ray fluorometry. The coloration of the copolymer was visually evaluated. Th results are shown in Table 4.

EXAMPLE 13

The procedures of Example 9 were essentially repeated except that the polymerization activator was omitted. The results are shown in Table 4.

EXAMPLE 14

The procedures of Example 9 were essentially repeated except that 1-butene as the α-olefin was used in place of propylene that and a deaerated aqueous alkaline solution was used. The results shown in Table 4.

COMPARATIVE EXAMPLES 4 AND 6

The procedures of Example 9 or 10 was essentially repeated except that deaerated pure water containing no air was used in place of air-saturated water used in Example 12 or 13. The results are shown in Table 4.

Table 3

	Example			Comp. Ex.
	9	10	11	4
Aqueous alkaline solution(1)				
Alkaline compound	NaOH	NaOH	NaOH	omitted
Concentration (mol/ℓ)	1.25	2.50	2.50	0
pH	>14	>14	>14	7
Amount of aqueous alkaline solution (ml)	200	10	2	0
Amount of additionally added pure water(2) (ml)	500	500	500	500
O_2 fed/equivalent O_2(3)	7	5	5	5
pH of aqueous phase after separation of oily phase and aqueous phase (pH)	13.4	12.4	11.4	4.0
Evaluation of copolymer after purifying				
V_2O_5 (ppm)	<1	<1	<1	15
Al_2O_3 (ppm)	6	4	25	77
Cl (ppm)	20	24	28	47
Color	white	white	white	pale yellow

(1), (2): Air-saturated water was used.

(3): Equivalent O_2: Amount of O_2 required for oxidizing vanadium to a pentavalent state.

The treatment with the aqueous alkaline solution and the separation of oily phase and aqueous phase were carried out at 60°C under a pressure of 0 kg/cm^2G.

Table 4

	Example			Comp. EX.	
	12	13	14	5	6
Amount fed during polymerization					
Solvent (ℓ/Hr)	4.1	7.3	4.9	3.4	5.2
Ethylene (g/Hr)	910	590	622	660	430
α-Olefin (a) (g/Hr)	1630	2220	545	1120	1610
Vandium compound (b) (mmol/Hr)	0.32	5.7	0.14	0.23	4.10
Organoaluminum compound (c) (mmol/Hr)	6.8	22.2	4.0	4.8	16.1
Polymerization activator (d)	0.28	omitted	0.13	0.20	omitted
Polymerization temperature (°C)	50	40	60	50	40
Aqueous alkaline solution(1)					
Alkaline compound	NaOH	NaOH	NaOH	NaOH	NaOH
Concentration (mol/ℓ)	0.16	0.41	0.30	0.16	0.50
pH	13.2	13.6	13.5	13.2	13.7
Amount of aqueous alkaline solution (ℓ/Hr)	0.2	0.2	0.2	0.2	0.2
Pure water added(2) (ℓ/Hr)	5	5	5	5	5
O_2 fed/equivalent O_2(3)	17	2	35	~0	~0
pH of aqueous phase after separation of oily phase and aqueous phase (pH)	10.4	10.4	11.0	10.6	10.8

Table 4 (cont'd)

	Example			Comp. EX.	
	12	13	14	5	6
Evaluation of copolymer after purifying					
V_2O_5 (ppm)	<1	2	<1	6	35
Al_2O_3 (ppm)	9	11	3	22	15
Cl (ppm)	9	<1	3	10	<1
Color	white	white	white	light gray	grayish green

(a): Butene-1 in Example 14 and propylene in other Examples.

(b): Vanadium oxytrichloride

(c): Ethylaluminum sesquichloride

(d): BPCC

(a): Air-saturated water was used in Examples 12 and 13. Deaerated water was used in Example 14 and Comparative Examples 5 and 6.

(2): Air-saturated water was used in Examples 12 to 14. Deaerated water was used in Comparative Examples 5 and 6.

(3): Equivalent O_2: Amount of O_2 required for oxidizing vanadium to a pentavalent state.

The treatment with the aqueous alkaline solution and the separation of the oily phase and the aqueous phase were carried out at 70°C under a pressure of 3 kg/cm^2G.

Claims

1. A method of purifying an ethylene-α-olefin copolymer obtained by polymerizing ethylene with an α-olefin having at least 3 carbon atoms, optionally with a non-conjugated diene compound, in a hydrocarbon solvent in the present of a catalyst comprising a vanadium compound, an organoaluminum compound, and a halogenated ester compound, said method comprising mixing and stirring a polymerization reaction mixture obtained by the polymerization reaction in an aqueous alkaline solution in such an amount as to give an aqueous phase having a pH of not lower than 10.0 after mixing and stirring.

2. A method as claimed in Claim 1, wherein said mixing and stirring comprises:
   a first step wherein the mixing and stirring of the polymerization reaction mixture obtained by the polymerization reaction is carried out in an aqueous solution containing an alkaline compound in such an amount that an aqueous phase separated in the subsequent second step has a pH of not lower than 10.0; and
   a second step wherein the mixture obtained in the first step is separated into an aqueous phase and an organic phase, and the organic phase is washed with neutral water.

3. A method as claimed in Claim 2, wherein said second step comprises:
   (a) 1/5 to 10 parts by volume of neutral water is mixed with one part by volume of the mixture obtained in the first step; and
   (b) the mixture obtained in the second step is separated into an aqueous phase and an organic phase, and the organic phase is washed with neutral water.

4. A method of purifying an ethylene-α-olefin copolymer obtained by polymerizing ethylene with an α-olefin having at least 3 carbon atoms, optionally with a non-conjugated diene compound, in a hydrocarbon solvent in the presence of a catalyst comprising a vanadium compound and an organoaluminum compound and optionally a halogenated ester compound, said method comprising an oxidation treatment of the polymerization reaction mixture obtained by the polymerization reaction in an aqueous alkaline solution in such an amount that an aqueous phase obtained after the oxidation treatment has a pH of not low r than 10.0.

5. A method as claimed in Claim 4, wherein said oxidation treatment comprises:
   a first step wherein the oxidation treatment of the polymerization reaction mixture obtained by th polymerization reaction is carried out in an aqueous solution containing (i) an oxidizing agent in at least a stoichiometric amount required for oxidizing vanadium present in said mixture to a pentavalent state and (ii) an alkaline compound in such an amount that an aqueous phase separated in the subsequent second stage has a pH of not lower than 10.0; and
   a second step wherein the mixture obtained in the first step is separated into an aqueous phase and an organic phase, and the organic phase is washed with neutral water.

6. A method as claimed in Claim 4, wherein said oxidation treatment comprises:
   a first step wherein the oxidation treatment of the polymerization reaction mixture obtained by the polymerization reaction is carried out in an aqueous solution containing (i) an alkaline compound in such an amount that an aqueous phase formed in the subsequent second step has a pH of not lower than 10.0;
   a second step wherein 1/5 to 10 parts by volume of water containing (ii) an oxidizing agent in at least a stoichiometric amount required for oxidizing vanadium present in said mixture to a pentavalent state is added to one part by volume of water obtained in the first step; and
   a third step wherein the mixture obtained in the second step is separated into an aqueous phase and an organic phase, and the organic phase is washed with neutral water.

7. A method as claimed in Claim 4, 5 or 6, wherein said oxidizing agent is oxygen.

8. A method as claimed in any preceding claim, wherein said vanadium compound is selected from VCl_3, VCl_4, $VOCl_3$, and $VO(OR)_{3-m}Cl_m$, wherein R is a straight or branched alkyl group, a cycloalkyl group, or an aryl group, each having 1 to 10 carbon atoms; and $3 \geqq m \geqq 0$.

9. A method as claimed in any preceding claim, wherein said organoaluminum compound is selected from AlR'_nCl_{3-n} and $AlR'_n(OR')_3$, wherein R' is a straight chain or branched alkyl group having 1 to 8 carbon atoms; and $3 \geqq m \geqq 0$.

10. A method as claimed in any preceding claim, wherein said halogenated ester compound is represented by the formula:

$$R'' - \underset{\underset{O}{\|}}{C} - O - R'''$$

wherein R" represents an organic group having 1 to 20 carbon atoms, which is partially or wholly substituted by a halogen atom; and R‴ represents a hydrocarbon group having 1 to 20 carbon atoms.